

comprises all of the  $\text{SiO}_2$  phase, the  $\text{SiC}$  phase, and/or the  $\text{SiB}_4$  phase, the  
aforementioned functions are effectively obtained.

The present invention can provide a carbonaceous material in which the  
charge-discharge capacity is improved and the degeneration of cycle-life characteristics  
is prevented by suppressing the volumetric expansion of the Si particulate, the  
separation of complex particles from the graphite particle, and the atomization of Si  
particulate caused by volumetric expansion upon charging.

The present invention can also provide a lithium secondary battery in which the  
energy density and cycle-life characteristics are improved by employing the  
carbonaceous material of the present invention as a negative electrode material.

While the present invention has been described in detail with reference to the  
preferred embodiments, those skilled in the art will appreciate that various modifications  
and substitutions can be made thereto without departing from the spirit and scope of  
the present invention as set forth in the appended claims.

**WHAT IS CLAIMED IS:**

1. A carbonaceous material comprising:

a graphite particle having a 002 plane interval  $d_{002}$  of less than 0.337 nm, as  
measured by the X-ray wide angle diffraction method;

a complex particle disposed and distributed in the vicinity of the surface of the  
graphite particle, the complex particle comprising silicon and carbon and having a  
particle size smaller than that of the graphite particle; and

an amorphous carbon layer having a 002 plane interval  $d_{002}$  of more than 0.37  
nm, as measured by the X-ray wide angle diffraction method, the amorphous carbon

layer being a polymer layer and being coated on the graphite particle and the complex particle rendering them bound;

wherein the complex particle comprises a Si particulate, a conductive carbon material disposed and distributed in the vicinity of the surface of the Si particulate, and a rigid carbon material layer coated on the Si particulate and the conductive carbon material rendering them bound, the Si particulate being composed of a crystalline Si phase.

2. The carbonaceous material according to claim 1, wherein the crystalline Si phase is deposited with at least one phase selected from SiO<sub>2</sub> phases, SiC phases, and SiB<sub>4</sub> phases.

3. The carbonaceous material according to claim 1, wherein the silicon and the carbon are present in a weight ratio of 0.1:99.9 to 50:50.

4. The carbonaceous material according to claim 2, wherein the  $P_{\text{SiO}_2}/P_{\text{Si}}$  ratio is no less than 0.005 and no more than 0.1 and the  $P_{\text{SiC}}/P_{\text{Si}}$  ratio is no less than 0.005 and no more than 0.1, wherein  $P_{\text{Si}}$  is defined as the diffraction intensity of the plane (111) of the Si phase,  $P_{\text{SiO}_2}$  is defined as the diffraction intensity of the plane (111) of the SiO<sub>2</sub> phase, and  $P_{\text{SiC}}$  is defined as the diffraction intensity of the plane (111) of the SiC phase, measured by the X-ray wide angle diffraction method.

5. The carbonaceous material according to claim 2, wherein the  $P_{\text{SiO}_2}/P_{\text{Si}}$  ratio is no less than 0.005 and no more than 0.1, the  $P_{\text{SiC}}/P_{\text{Si}}$  ratio is no less than 0.005 and no more than 0.1, the  $P_{\text{SiB}}/P_{\text{SiO}_2}$  ratio is no less than 0.1 and no more than 5.0, and a  $P_{\text{SiB}}/P_{\text{SiC}}$  ratio is no less than 0.1 and no more than 5.0, wherein  $P_{\text{Si}}$  is defined as the diffraction intensity of the plane (111) of the Si phase,  $P_{\text{SiO}_2}$  is defined as the diffraction

intensity of the plane (111) of the  $\text{SiO}_2$  phase,  $P_{\text{SiC}}$  is defined as the diffraction intensity of the plane (111) of the SiC phase, and  $P_{\text{SiB}}$  is defined as the diffraction intensity of the plane (104) of the  $\text{SiB}_4$  phase, as measured by the X-ray wide angle diffraction method.

6. The carbonaceous material according to Claim 1, wherein the graphite particle has a particle size ranging from 2 to 70  $\mu\text{m}$ , the complex particle has a particle size of no less than 50 nm and no more than 2  $\mu\text{m}$ , and the amorphous carbon layer has a thickness of no less than 50 nm and no more than 5  $\mu\text{m}$ .

7. The carbonaceous material according to claim 1, wherein the Si particulate has a particle size of no less than 10 nm and less than 2  $\mu\text{m}$ , the conductive carbon material has a specific resistance of no more than  $10^{-4} \Omega \cdot \text{m}$ , and the rigid carbon layer has a flexibility strength of no less than 500  $\text{kg}/\text{cm}^2$  and a thickness of no less than 10 nm and no more than 1  $\mu\text{m}$ .

8. The carbonaceous material according to claim 1, wherein the complex particle is present in an amount no less than 1% by weight and no more than 25% by weight.

9. The carbonaceous material according to claim 1, wherein the amorphous carbon layer is obtained by heat-treating at least one polymer material selected from the group consisting of thermoplastic resins, thermosetting resins, vinyl-based resins, cellulose-based resins, phenol-based resins, coal-based pitch materials, petroleum-based pitch materials, and tar-based materials.

10. The carbonaceous material according to Claim 9, wherein the mixing weight ratio of Si : graphite : polymer is 0.1:99.8:0.1 to 40:40:20.

11. A lithium secondary battery comprising the carbonaceous material according to Claim 1.

12. A method of preparing a carbonaceous material comprising the steps of:

5        calcining a Si particulate composed of a crystalline Si phase in a carbon crucible at 1300to1400 °C to deposit a SiO<sub>2</sub> phase and a SiC phase in the crystalline Si phase;

         adding a conductive carbon material to the Si particulate;

         applying a polymer material coating solution to the Si particulate to provide a complex particle precursor;

         calcining the complex particle precursor to render the polymer material coating solution into a rigid carbon layer to provide a complex particle;

         adding the complex particle to a graphite particle;

         applying a polymer material coating solution to the graphite particle to provide a carbonaceous material precursor; and

         calcining the carbonaceous material precursor to render the polymer material coating solution into an amorphous carbon layer to provide a carbonaceous material.

13. A method of preparing a carbonaceous material comprising the steps of:

20        calcining a Si particulate together with a B<sub>2</sub>O<sub>3</sub> powder in a carbon crucible at 1300to1400 °C to deposit SiO<sub>2</sub>, SiC, and SiB<sub>4</sub> phases in a crystalline Si phase;

         adding a conductive carbon material to the Si particulate;

applying a polymer material coating solution to the Si particulate to provide a complex particle precursor;

calcining the complex particle precursor to render the polymer material coating solution into a rigid carbon layer to provide a complex particle;

5 adding the complex particle to a graphite particle;

applying a polymer material coating solution to the graphite particle to provide a carbonaceous material precursor; and

calcining the carbonaceous material precursor to render the polymer material coating solution into an amorphous carbon layer to provide a carbonaceous material.

2010E014248001